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Effect of Ag Doping on Optical Constant and Hall Effect Measurements of SnS Thin Films

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Abstract. In this report Silver doped Tin Sulfide (SnS) thin films with ratio of (0.03) were prepared using thermal evaporation with a vacuum of $4*10^{-6}$ mbar on glass with (400) nm thickness and the sample annealing with (573K). The optical constants for the wavelengths in the range (300-900) nm and Hall effect for (SnS and SnS:3% Ag) films are investigated and calculated before and after annealing at 573 K. Transition metal doped SnS thin films the regular absorption 70% in the visible region, the doping level intensification the optical band gap values from 1.5- 2 eV. Silver doped tin sulfide (SnS) its direct optical band gap. Hall Effect results of (SnS and SnS:3% Ag) films show all films were (p-type) electrical conductivity with resistivity of 6.91×10^{1} Ω cm , and both Hall mobility and the carrier concentration varies after doping and annealing. Hole concentration increase from 3.7×10^{13} to 2.94×10^{14} cm^{-3} and hole mobility of 2.42×10^{3} $cm^2/(V\ s)$. Doping with Ag lead to properties with characteristics suitable for solar cell application

Keywords: Tin sulfide, optical constant, annealing, Ag doping, Hall effect.

INTRODUCTION

Midst the metal sulfde semiconductors, tin sulfde (SnS) is an IV–VI group, p-type, low band gap (1.2–1.6 eV) semiconductor with a high absorption coefficient of~10^4 cm^{-1} in the visible and near-infrared (NIR) region for constructing optoelectronic devices [1]. (SnS) become one of the record researched semiconductor materials due to the great promise it has shown in the numerous technological applications such as absorber layers in hetero junction solar cells [2], photo detectors [3], Schottky diodes [4], optoelectronic switches [5], and gas sensors [6]. The basic mechanism is the creation of an electron-hole pair by exciting an electron from the valence to the conduction band through light absorption that exceeds the band gap energy [7]. Due to special properties such as easy availability in nature, inexpensiveness [8], high absorption coefficient, wide excitation spectra, and huge charge carriers per photon for solar, tin sulfde constitutes a very valuable material for optical applications [9]. Doping is considered by means of an operative way to advance the structural, optical, and electrical properties of the materials due to the creation of defects. Additionally, SnS was doped with quite a few elements for example indium (In) , copper (Cu) , aluminum (Al) , silver (Ag) , lead (Pb) and sodium (Na) to improve the properties of the sample [10-15]. The influence of altered material dopant on SnS characterization thin were explored by various researches via dissimilar technique of preparation such as the Eg decreases and absorption coefficients increasing from optical studies of Cu:SnS films were well fabricated by thermal evaporation technology [16] and Nanostructured SnS thin film pure and doped-In was deposited on fluorine-doped tin oxide (FTO) substrates by electrochemical deposition technique, decreases of energy gap (Eg) with the doped (In) thin films, [17]. In tin sulfide thin films, loferski theoretically proved that a maximum efficiency of 25% is achievable for this material [18]. Researchers used different method to preparation SnS films like RF-Sputtered [8], chemical bath deposition [10], thermal evaporation [11], spray pyrolysis method[13], hot wall method[14] and others.

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The aim of this work is to produce high-quality Ag –doped (SnS) thin films after preparation thin films by thermal evaporation technique for optical application. Unusual consideration was remunerated to the influence of the processing parameters, such as dopant concentration and annealing temperature into the targets of the films during the deposition.

EXPERIMENTAL

SnS thin films are obtained after preparation of the alloy, SnS alloy obtained by great purity (99.999%) tin (Sn) & sulfide (S) elements with weight percentages (1:1) formerly put these elements in tube of quartz with pressure (4×10^{-4} mbar), subsequently that (Sn) and (S) located at temperature (1000 K) in an electric oven for five hours, the mixture left to cool slowly. The SnS thin films were synthesized by thermal evaporation technique in a high vacuum system of ($3x10^{-6}$) torr on glass. The substrates from molybdenum boat using Edward coating unit model (E 306) and cleaned by DI water and acetone in an ultrasonic bath and dried by air.

Thickness of film was (400) nm, doped ratio of A g w a s 3 % and deposition rate (1 nm/sec), the distance between the substrate and boat was about 16 cm. The sample annealed at (573) K for about one hour. UV/Visible 1800 spectrophotometer used to study the optical properties for films deposited on glass substrates from (300- 1100) nm. From Hall Effect resistivity, conductivity type, Hall mobility and carrier concentrations were calculated using Van der Pauw Ecopia-HMS -3000.

RESULTS AND DISCUSSION

The influence of annealing temperature 573 K on the optical properties of (SnS and SnS:3% Ag) thin films deposited on glass substrates are studied deeply. The variation of absorbance and the absorption coefficient (α) of (SnS and SnS:3% Ag) films before and after annealing is shown in Figure (1 and 2), where a decrease in absorption coefficient after doping within all the range of the spectrum.. It could be seen that all the films exhibits high values of absorption coefficient ($\alpha > 10^5$ cm^{-1}) which means that allowed direct transition for these films. The optical energy gap (Egopt) values which calculated from Tauc equation [19, 20] by plotting the relation $(\alpha h\nu)^2$ versus photon energy (hν) as shown in fig (3). It is clear that the Eg^{opt} increased from (1.5 eV) to (2 eV) when doped films with 3% Ag.

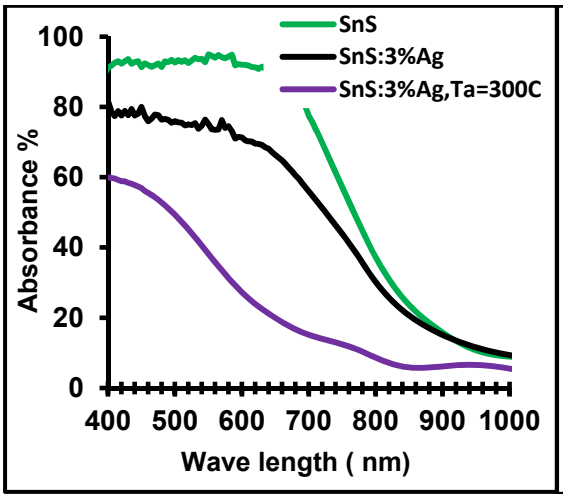

FIGURE 1. SnS thin film absorption as wavelength.

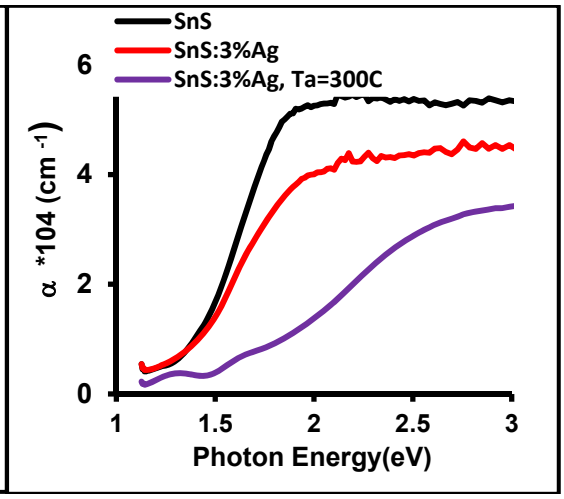

FIGURE 2. The relation between the absorption function of coefficient and photon energy for SnS films.

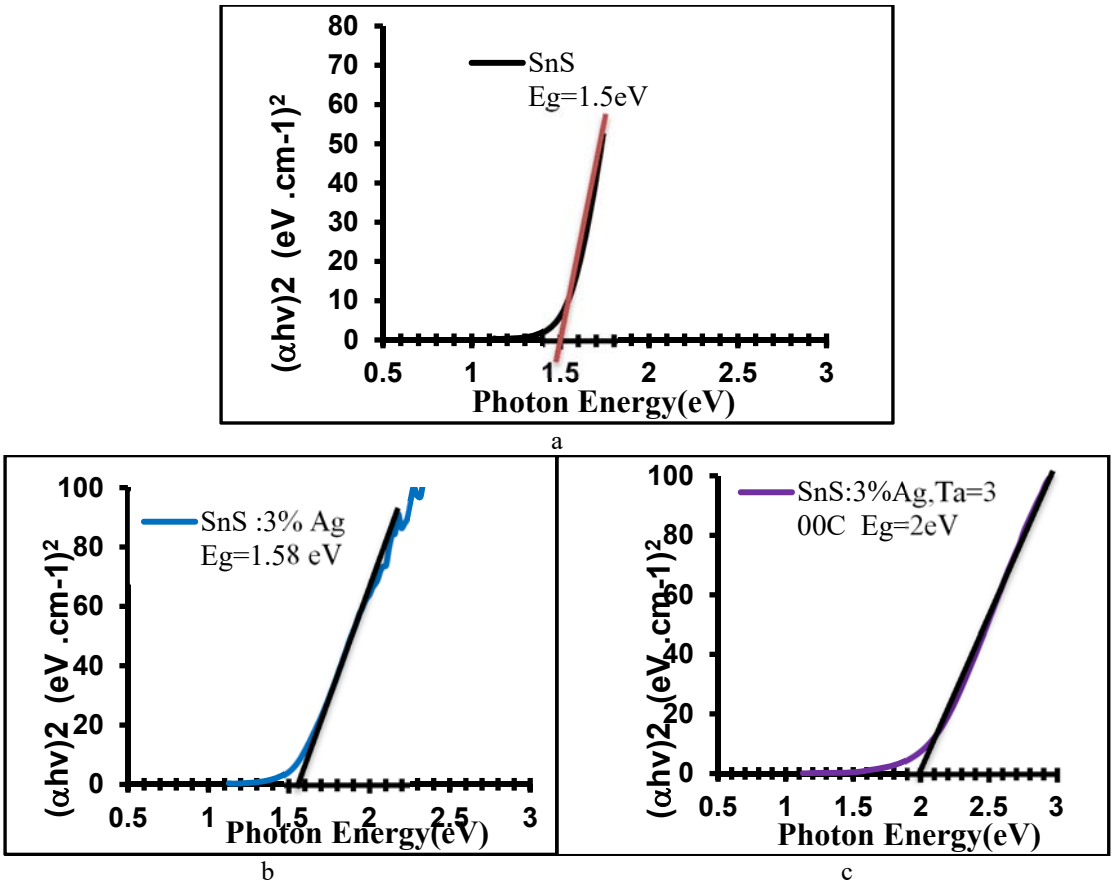

FIGURE 3. (αhv)2 and photon energy for SnS thin films. a) pure b) 3 % Ag doped at R.T , b) 3% Ag doped at (Ta=573 K) .

The variation of the refractive index values (n) versus photon energy (hν) for (SnS and SnS:3% Ag) films before and after annealing which calculated from reflectance [21] as given in Fig (4), it is clear from result that the refractive index values increase doping, this behavior may be due to more packing density because improvement in the films structure. Extinction coefficient (k) versus photon energy is shown in Fig (5) for (SnS and SnS:3% Ag), the decrease in extinction coefficient values after doping is similar the absorption coefficients behavior.

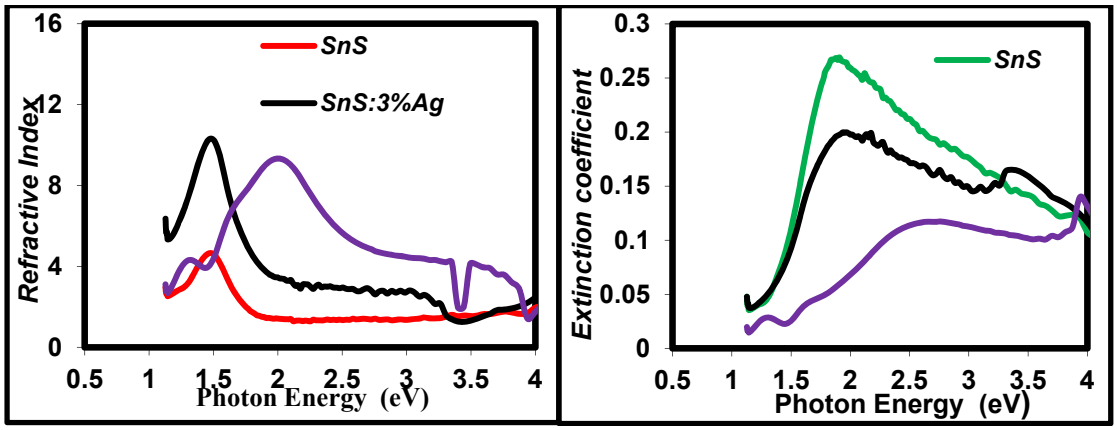

FIGURE 4. Variation of refractive index versus photon energy of SnS thin films.

FIGURE 5. Extinction coefficient as a function of photon energy of SnS thin films.

Fig (6 a, b) shows the effect of doping by Ag on the values of the real (ε_1) and imaginary (ε_2) parts of the dielectric constant. From this figure we can notice that the real part of the dielectric constant (ε_1) increase depend mainly on the value of the refractive index while the imaginary part of the dielectric constant (ε_2) showed an opposite trend after doping depend on the extinction coefficient values.

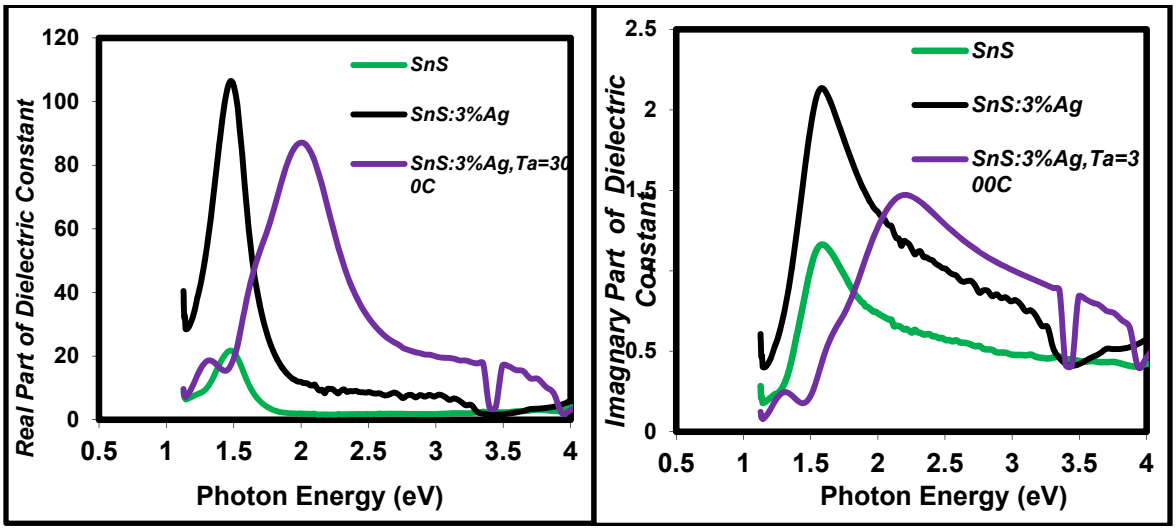

FIGURE 6. a) The real part b) imaginary part of the dielectric constant versus photon energy for SnS thin films.

The Hall coefficient values (R_H) were evaluated for (SnS and SnS:3% Ag) films which is used to determined Hall mobility (μ_H) and carrier density(n_H) [22]. All SnS films exhibit p-type conductivity due to the sign of Hall coefficient is positive which means the holes are majority charge carriers in the conduction process. All these parameters are shown in Table 1.

TABLE 1. Hall parameter for SnS thin films

Sample	Ta K	R_H	N_A cm^{-3}	μ_H (cm^2/ V.S)	ρ (Ω.cm)
SnS	R.T	1.002×10^8	3.7×10^{13}	2.42×10^3	6.914E+1
	573	1.65×10^8	6.2×10^{10}	1.29×10^3	1.527E+4
SnS:3%Ag	R.T	2.12×10^6	2.94×10^{14}	2.53×10^3	8.354E+2
	573	2.21×10^6	2.82×10^{14}	9.29	2.379E+5

It is clear from Table 1 that both (n_H) and (μ_H) for SnS varies after doping with Ag. This behavior can be attributed to the decrease grain boundary scattering and the trapping centers of charge carriers because of the improved film structure after doping.

CONCLUSION

In research, thermal evaporation method used to study (SnS and SnS:3% Ag) films with thickness of 400 nm through measurements of optical properties and Hall Effect. A thermal evaporation was a good method to prepare (SnS and SnS:3% Ag) films from alloy. All optical constant change after doping and give good films for solar cell application. The optical energy gap increase from 1.5 to 2 eV after doping and annealing at 573K. Among the fabricated thin films, the sample doped with Ag reveals the highest transmittance. Hall Effect measurements confirmed that holes were predominating in the conduction process, higher mobility and carrier concentrations was noted for sample doped with 3% Ag.

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